B.Sc. Semester-VI
Group-A / DSE-4
Organic Synthesis

III. Photochemistry

5. Arene-Alkene Photocycloaddition Reaction

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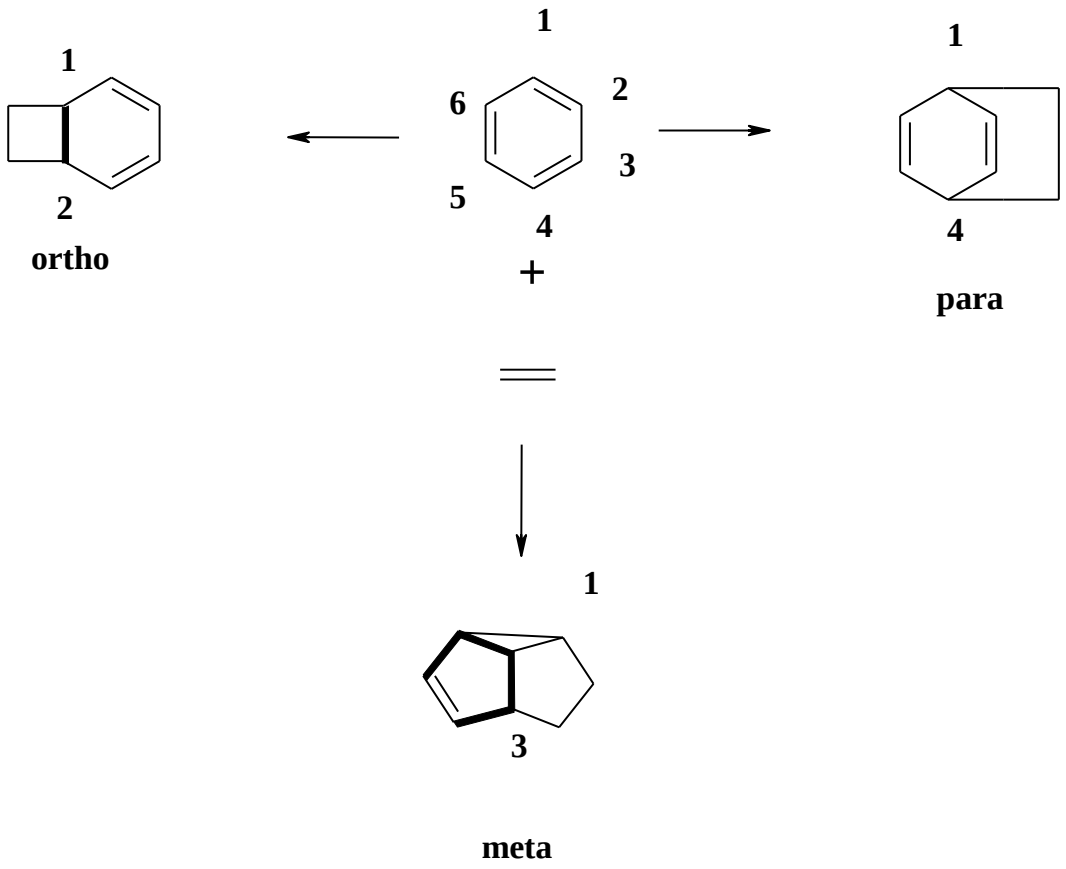
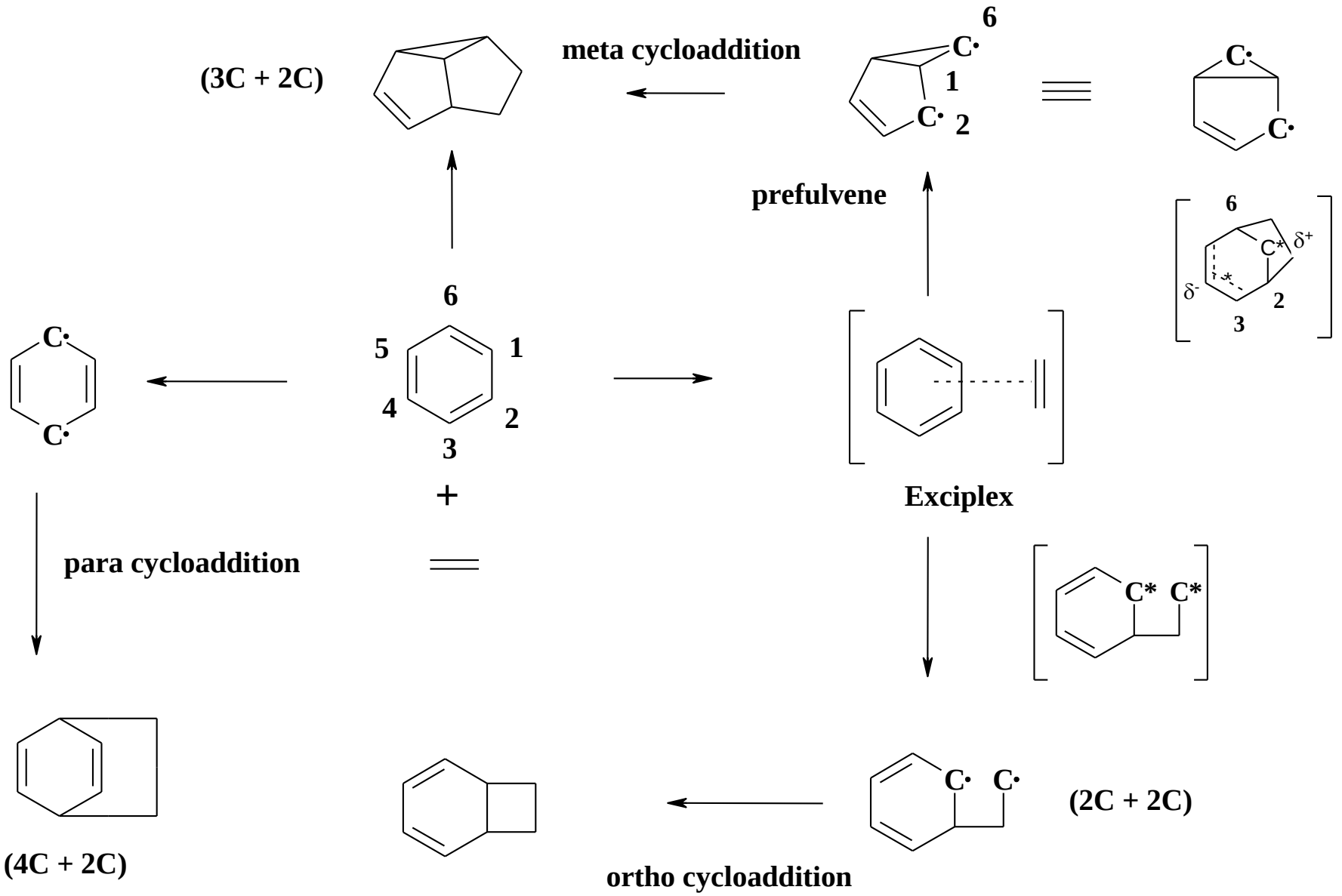


Possible modes of addition in the arene-alkene photocycloaddition reactions



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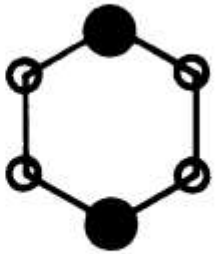
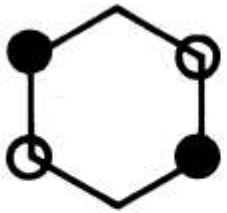
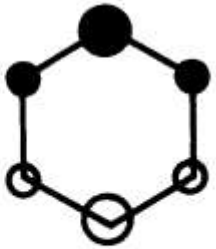
Mechanistic proposal for the arene-alkene photocycloaddition reaction



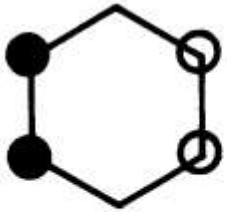
S^*



A^*



S

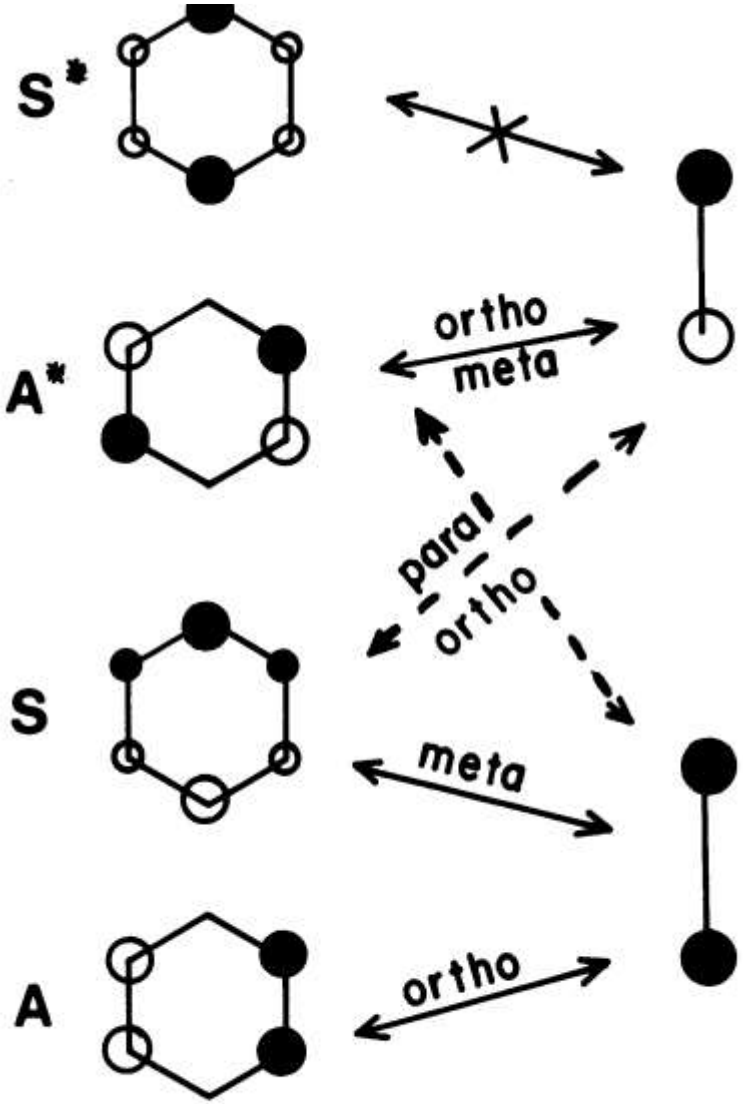


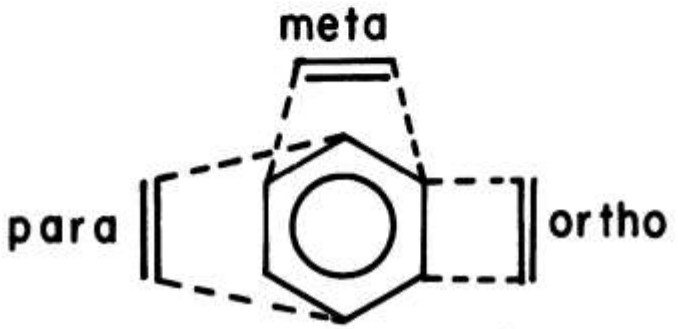
A

One electron configurations: SS^*, AA^*, SA^*, AS^*

States:
- B_{2u} ($SA^* - AS^*$) lowest excited singlet state
- B_{1u} ($SS^* + AA^*$) lowest triplet state
- E_{1u} ($SS^* - AA^*$; $SA^* + AS^*$) degenerate states

Fig. 4. Frontier molecular orbitals, excited configurations, and excited states of benzene.





$r_{ortho} = 1.395$ Å

$r_{meta} = 2.416$ Å

$r_{para} = 2.790$ Å

Fig. 7. The benzene-ethylene orbital interactions hich lead to excited singlet state stabilization.

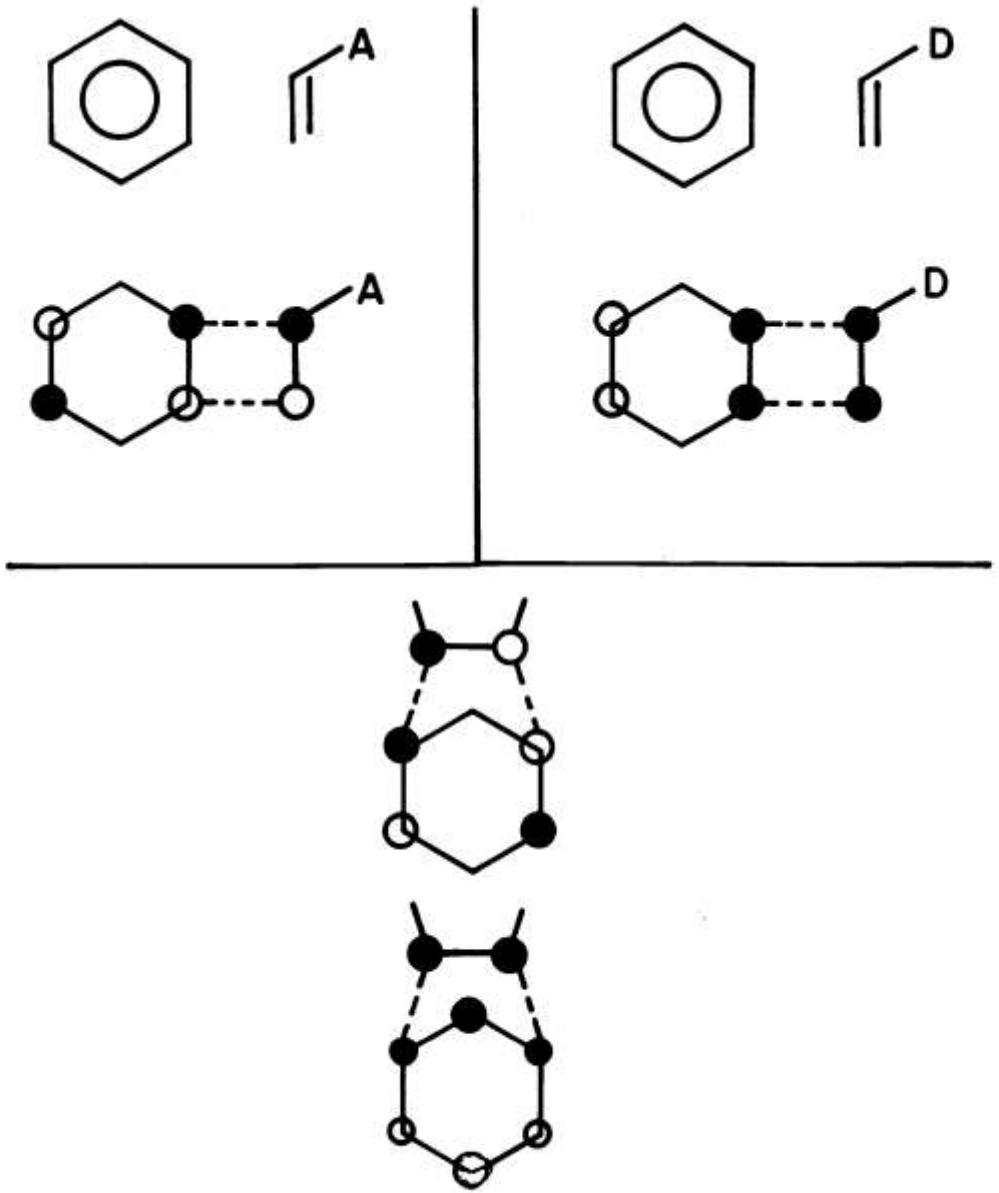
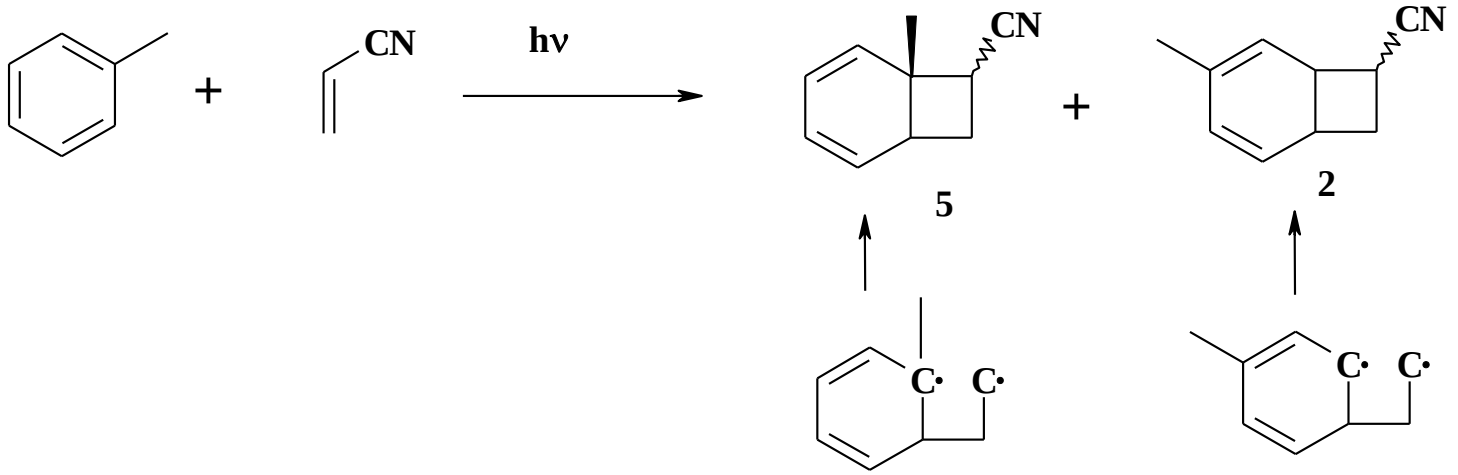
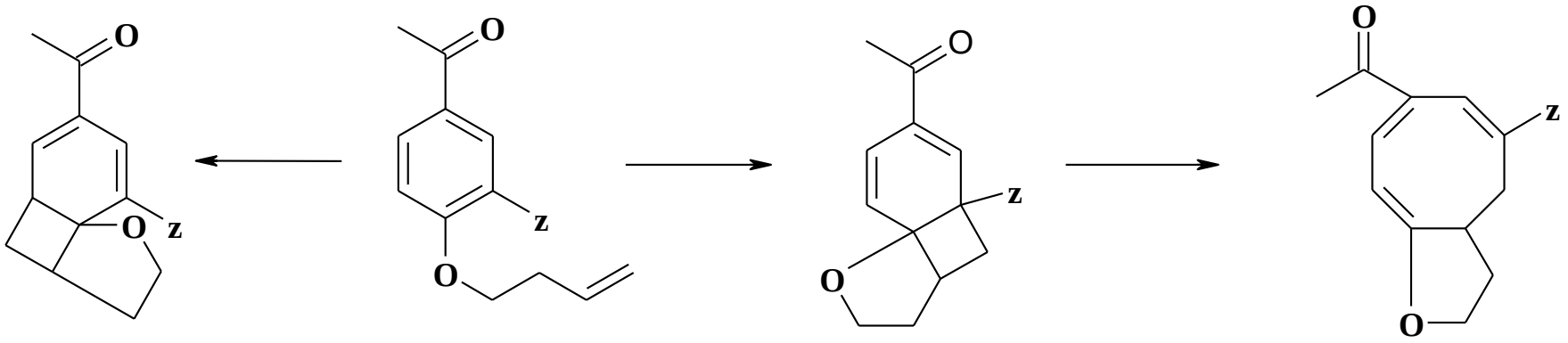


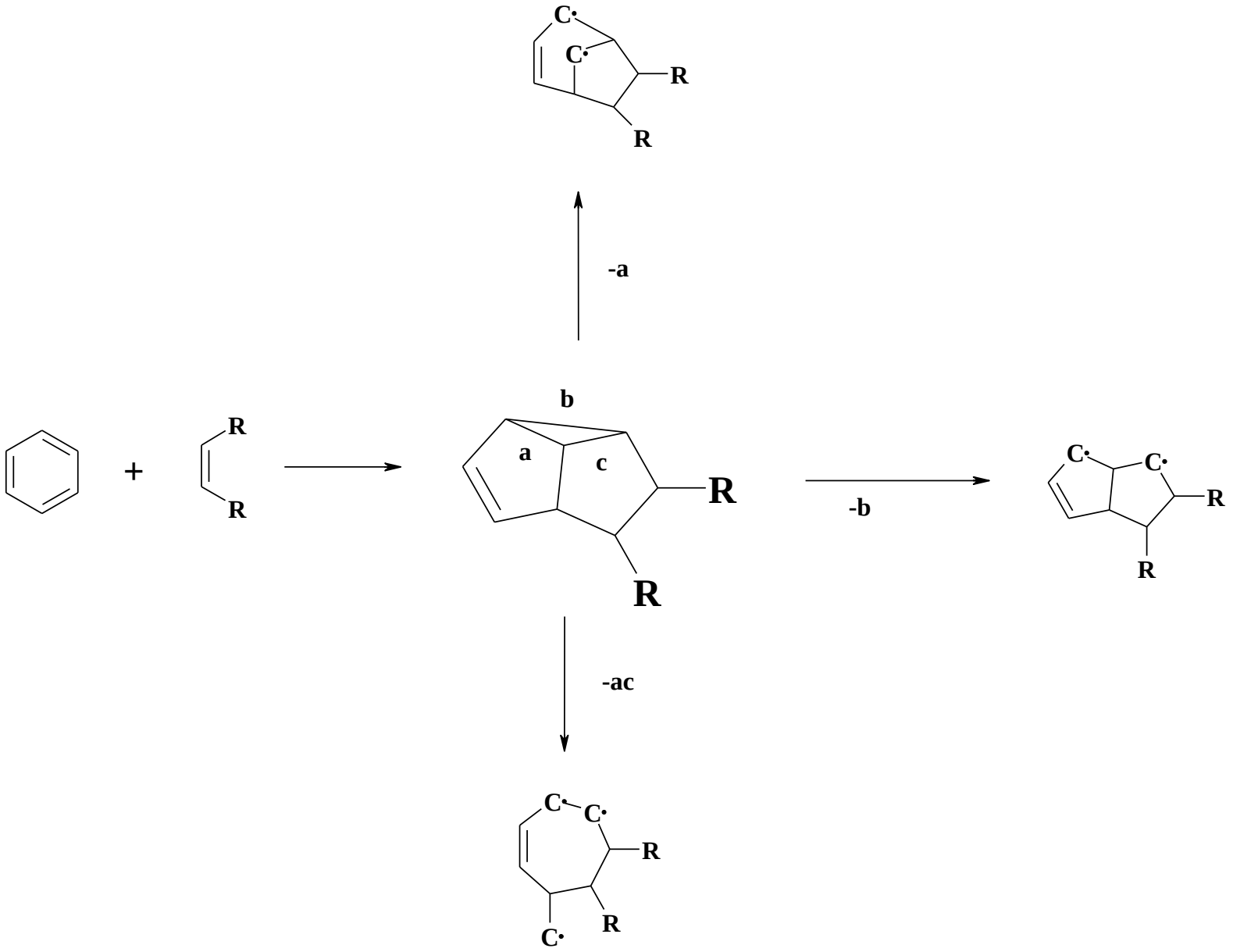
Fig. 12. Orbital interactions which control cycloaddition periselectivity.



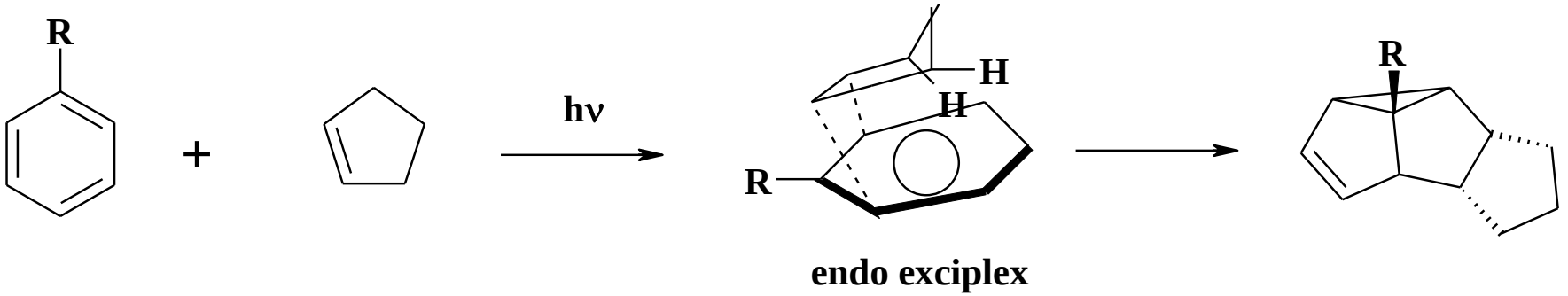


z = OMe

z = $CONH_2$, CN, Me



Possible mode of cleavage of the cyclophotoadduct



endo exciplex

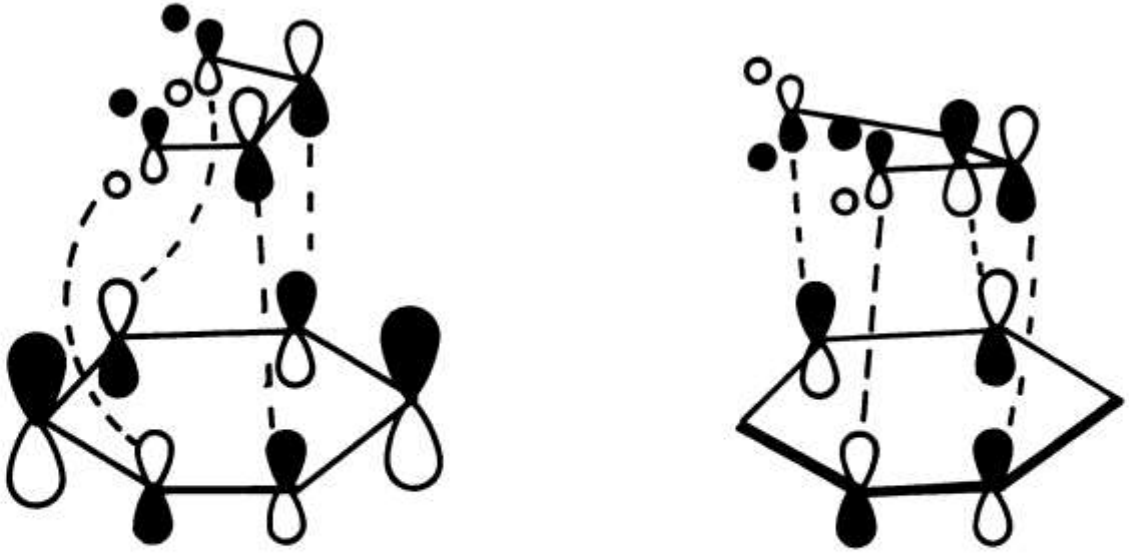
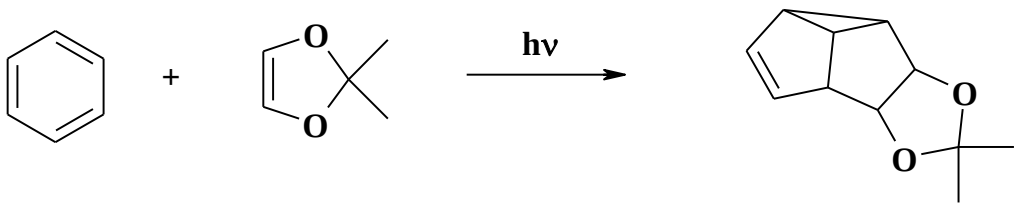
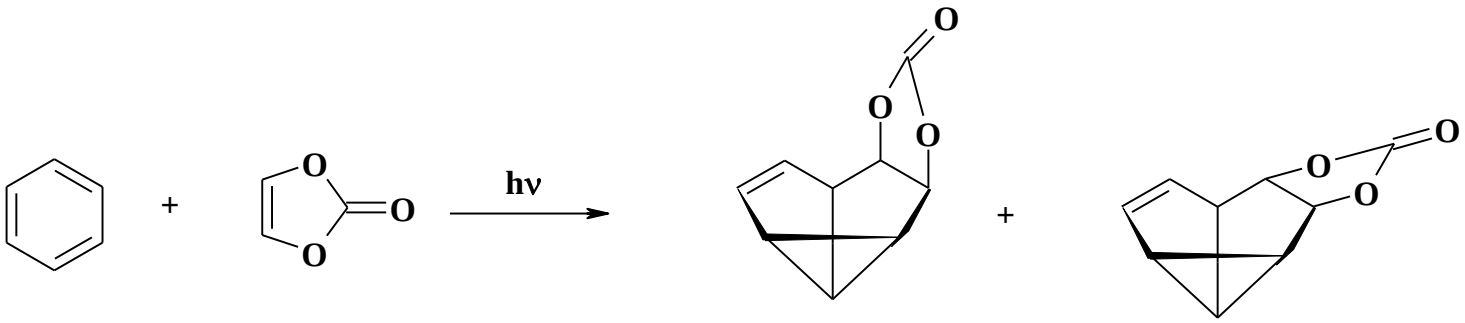


Fig. 15. Secondary orbital interactions which stabilize the endo complexes.



exo adduct

secondary orbital intercation is not favored due to presence of non bonded "O" electron

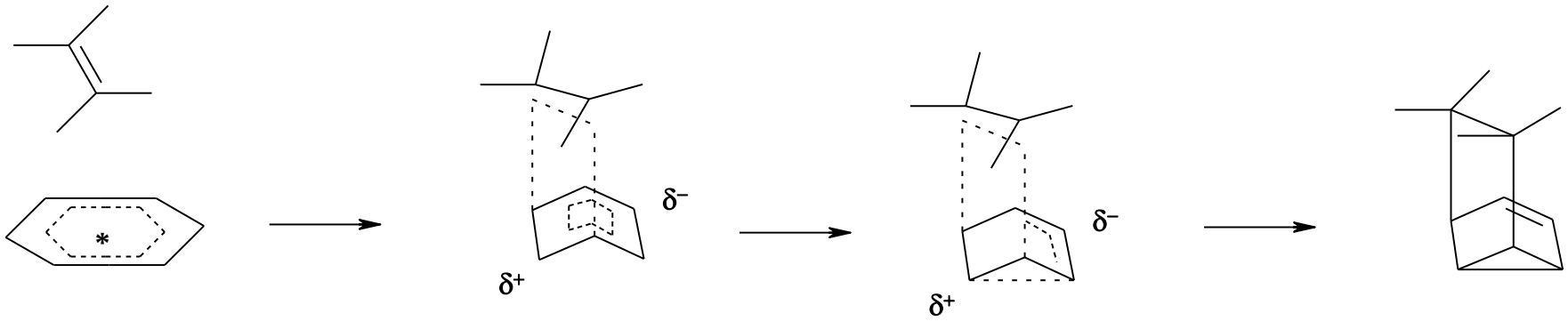


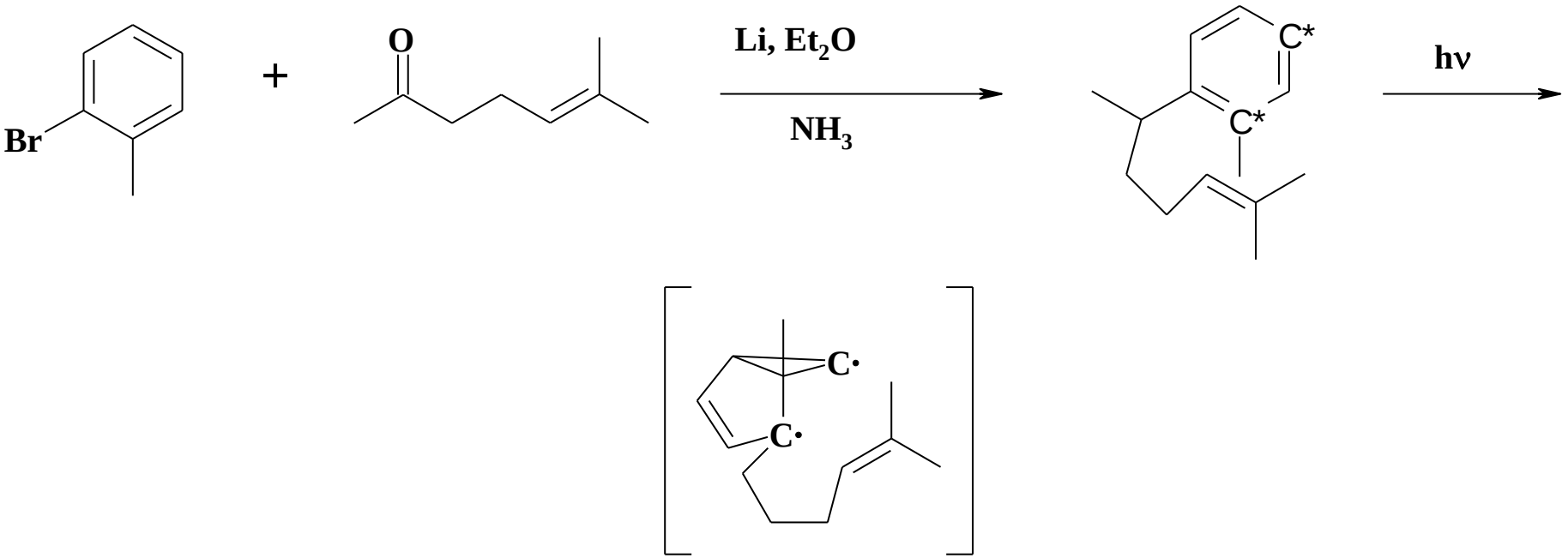
endo

5

exo

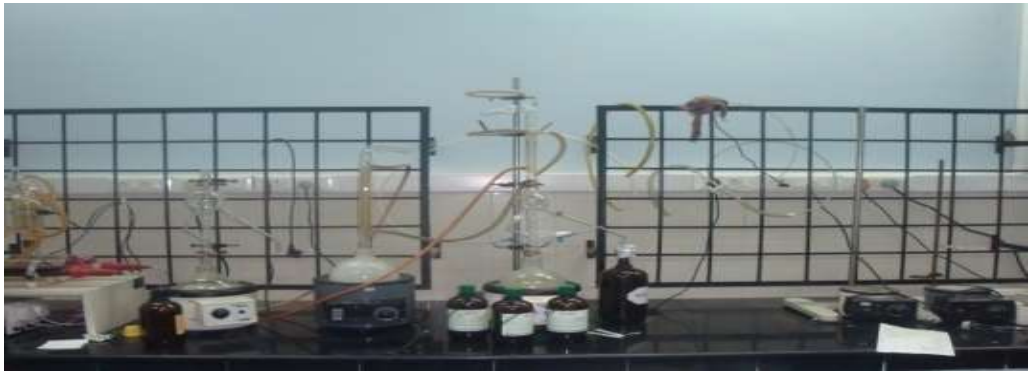
1





Silphene

Thank You



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